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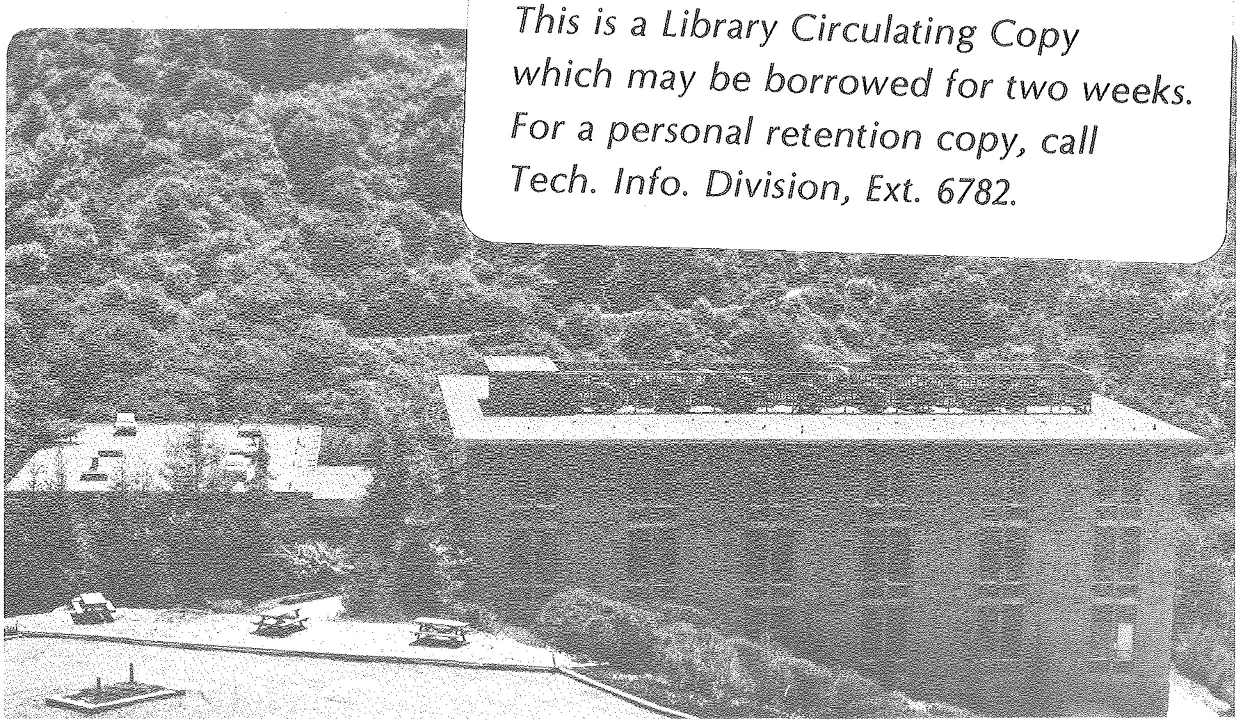

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A RADIOTRACER TECHNIQUE FOR ADSORPTION AND CATALYSIS STUDIES: APPLICATION TO ^{14}C-BENZENE CHEMISORPTION AND REHYDROGENATION ON Pt(111)

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ABSTRACT

A radiotracer counting system was developed for adsorption and catalysis studies in ultrahigh vacuum using small area, single crystal surfaces. The counting system utilizes a rugged, compact, and rotatable surface barrier detector with a sensitivity sufficient to detect about 1×10^{12} molecules containing carbon-14. The operating characteristics and performance of this counting system are discussed along with its application to studies of ^{14}C-benzene chemisorption and rehydrogenation on the (111) crystal face of platinum.

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Introduction

Radiotracer methods are among the most powerful techniques for measuring very low concentrations of materials in a transient environment. They are of particular value when studying the residence time of a surface layer in the presence of the same molecule in the gas phase as occurs in heterogeneous catalysis. While static radiotracer measurements directly determine the absolute adsorbate surface coverage on the catalyst, dynamic experiments can also be easily carried out to determine the kinetics of important surface phenomena such as isothermal desorption, bulk dissolution, surface diffusion, and exchange or rehydrogenation reactions of these adsorbed species. A distinction between the kinetics of intermolecular hydrogen transfer and direct rehydrogenation reaction steps, for example, should be very useful in establishing reaction mechanisms for Fischer-Tropsch synthesis and hydrocarbon reforming over metal catalysts. Since the adsorbed species which form during these reactions are hydrocarbon fragments that may be derived from readily available compounds labelled with carbon-14, radiotracers can provide a direct method for determining the reaction pathway.

While ^{14}C-radiotracers have been used by several groups to investigate the interactions of hydrocarbons with metal powders and supported metal catalysts (1-3), the radiotracer technique has found only limited application in adsorption studies that are carried out in ultrahigh vacuum (UHV) using well-defined surfaces. In studies of ^{14}CO chemisorption on nickel, Klier and his coworkers (4,5) described a thin window Geiger-Müller (GM) counter that could be used in vacuum systems at 10^{-10} Torr with a sensitivity sufficient to detect 10^{12} adsorbed molecules. A major problem in these studies was in mounting the detector in order to prevent the thin mica window from rupturing. In this report we describe an alternative method to detect ^{14}C-radiotracers which is simple, sensitive, rugged, and more versatile than the GM counter and is suitable for general surface studies. In our investigation a compact, rotatable surface barrier detector is used with conventional counting electronics to detect beta radiation emitted by ^{14}C-labelled hydrocarbons chemisorbed on platinum single crystal surfaces. The performance and capability of this system are discussed along with its application to studies of ^{14}C-benzene chemisorption and rehydrogenation on Pt(111).

Experimental

A block diagram showing the experimental arrangement and counting electronics for radiotracer studies is shown together with a cross section of a surface barrier detector in Figure 1. All experiments are carried out in a previously described (6) low pressure-high pressure apparatus that is used for combined surface analysis (LEED, AES, TDS) and catalysis studies. The base pressure of this system following bake-out is less than 1×10^{-9} Torr. The surface barrier detector (Ortec TA-23-25-300) is a large area diode consisting of a partially depleted slice of ultra-pure n-type silicon mounted in an insulating ring, the front and back surfaces of which are metallized. The entrance contact-surface barrier (gold window, 40 μg cm^{-2}) and depth of the depletion region (300 μm) are chosen to optimize the detector efficiency for low energy beta radiation (^{14}C-$E_{max} \simeq$ 158 KeV, range in Si $\simeq$ 150 μm). The front surface of the insulating ring is grounded to the metal case and to the shield side of a standard Microdot connector. The back surface of the ring contacts the center electrode of the connector which functions as a signal output and bias voltage connection. Free charge carriers created during operation by ionizing radiation are separated by an electric field that is produced by an externally applied reverse bias (50 V). Integration of the current induced on the detector contacts yields an output pulse that is proportional to the energy of the ionizing radiation (7). Output pulses are amplified and shaped by a charge sensitive preamplifier (Ortec 109) and linear amplifier (BNC MA-1). For point-by-point measurements, N(E) beta spectra are collected and stored in a multichannel analyzer (Tracor TN 1705). Energy scale is calibrated using the signal from a tail pulse generator (BNC RP2) applied to the preamplifier test input. Integration of the timed spectra yields a count rate that is proportional to the radioactivity present in the source. Alternatively, a ratemeter or multichannel scaler can be used for continuous measurements using an appropriately wide window ($\sim$35-158 keV).

A more detailed diagram of the detector mounting assembly is shown in Figure 2. The entire assembly, including the detector, an electrical connection, and provisions for water or nitrogen cooling, are easily accommodated on a single 6 inch (152 mm) conflat flange. The detector (case diameter $\sim$ 20 mm) is recessed into a copper jacket fixed to an L-shaped rotatable feedthru offset about 40 mm from the center of the 152 mm flange. The rotation mechanism allows the detector to be reproducibly aligned 5-10 mm directly in front of the crystal for counting adsorbed species or quickly rotated 90-180° for background corrections, high pressure reaction rate studies, or rapid interchange between other surface analysis methods. The output/bias connection from the detector to an external feedthru is made using a flexible 93Ω shielded cable. When bias is applied, the detector must be maintained at temperatures between -30 and 30°C. In practice, the background noise level can be minimized by operating the detector at about 15°C or less. Slight cooling of the detector is easily accomplished using two strips of flexible copper braid that are connected from the back-side of the copper jacket to an adjacent copper block that is cooled by circulating water or nitrogen.

Solid state detectors always display an appreciable level of low energy noise resulting from leakage current and random fluctuations in charge carrier density. This noise ordinarily amounts to 8-10 keV and must be discriminated against in order for quantitative analysis to be carried out. In practice, because of peak broadening in the preamplifier and amplifier, the lower discriminator level must be set at 2-3 times the detector noise level in order to eliminate all noise. This is illustrated in Figure 3, where N(E) beta spectra are compared at two lower discriminator energies for a 1 cm^2 sheet of ^{14}C-polymethylmethacrylate suspended in the vacuum chamber at the same position as the platinum single crystal. The left hand spectrum obtained with the discriminator set to about 10 keV displays a sharp low energy peak due to detector noise superimposed on a slowly decreasing background which represents the actual ^{14}C-beta emission. The right hand spectrum obtained with the discriminator set to about 35 keV displays the ^{14}C-beta spectrum with no contribution by detector noise. To determine the optimum operating conditions for the surface barrier detector in UHV, the count rates for background, and the ^{14}C-polymethylmethacrylate sheet were monitored as a function of the lower discriminator energy. The results are shown in Figure 4 where the ^{14}C-count rate (cpm) been squared, divided by the background count rate (Bkg), and plotted as a function of the lower discriminator energy. The maximum in cpm^2/Bkg ($\sim$32 keV) defines the operating conditions with maximum signal-to-noise. To provide an additional measure of noise rejection, all measurements described hereafter were carried out with the lower discriminator set to 35 keV. To determine how much of the ^{14}C-beta emission would be rejected by 35 keV, we used a liquid scinitalltion counter to plot an unquenched ^{14}C-beta spectrum and calculated from this that about 40% of the activity would be rejected.

As indicated in Figure 2, the active area of our detector (25 mm^2) is comparable to the crystal face surface area for a typical single crystal sample. The counting geometry for a point source located 10 mm from this active surface is 0.34 π. Fortunately, the detector efficiency can be calibrated in a manner which corrects for the discriminator level, the counting geometry, and the surface area of the crystal surface. In the efficiency measurements, the Pt(111) crystal face (0.22 $\pm$ 0.02 cm^2) was coated with several microliters of a solution (1.1 μg/ul; specific activity 4.56 dpm/ul) containing ^{14}C-polymethylmethacrylate dissolved in ethyl acetate. Evaporation of the solvent yielded thin uniform films (1.1-6.7 μm) of ^{14}C-polymethylmethacrylate coated onto the single crystal surface. The count rate for the polymer films was monitored as a function of film thickness providing the calibration curve shown in Figure 5, where the observed efficiency (cpm/dpm) is plotted as a function of film thickness. For the counting geometry and limited range of film thickness investigated, the counting efficiency was 2.9 $\pm$ 0.3%.

<u>Application to ^{14}C-Benzene Chemisorption and Rehydrogenation on Pt(111)</u>

To investigate the performance of the radiotracer technique, the chemisorption of ^{14}C-benzene in submonolayer amounts was studied on the

(111) crystal face of platinum. The ^{14}C-benzene was supplied by New England Nuclear Corp. ($\gtrsim$98% radiochemical purity) and possessed a specific radioactivity of 16$\pm$1 mc mmole^{-1}. The material was outgassed by repeated freeze-pumping cycles prior to use.

Absolute adsorbate surface concentrations determined from the rate of beta emission following low pressure exposures at temperatures ranging from 45-350°C are shown in Figure 6 ($1L=10^{-6}$ Torr sec uncorrected for ion gauge sensitivity). The error bars represent estimated uncertainties for the measurements that are based on the accuracy of the detector efficiency calibration and the specific radioactivity of the ^{14}C-benzene. Counting times for the measurements ranged from 15 to 40 minutes, and count rates for adsorbed species and background varied between 15 to 180 and 2 to 6 cpm, respectively. The level of background (chamber) activity increased gradually during a series of experiments, but always decreased to a low value of 2-3 cpm after outgassing overnight.

The surface concentration by adsorbed species increases with increasing temperature and exposure. Complementary UPS, TDS, LEED, and ^{14}C-radiotracer studies (8) revealed that irreversible, dissociative chemisorption occurs over most of this temperature range. Benzene chemisorbed on Pt(111) at $\sim$45-65°C displays the $\begin{vmatrix} 4 & -2 \\ 0 & 5 \end{vmatrix}$ diffraction pattern (9). One chemisorbed benzene molecule per unit cell corresponds to a surface concentration of 7.5×10^{13} molec cm^{-2}. This concentration agrees very well with that ($8\pm1\times10^{13}$ cm^{-2}) measured directly from the radiotracer analysis (Fig.6). The maximum surface coverage achieved after ^{14}C-benzene chemisorption at 350°C corresponds to 2.0 carbon atoms per surface platinum atom. While no ordering could be detected at temperatures between 80 and 350°C, it is notable that this maximum coverage approaches that expected for a close-packed graphitic overlayer with C/Pt=2.57.

The radioactivity of ^{14}C-labelled overlayers can be correlated with the peak-to-peak height intensity for the 273 eV carbon Auger transition to provide a convenient, absolute Auger calibration for surface carbon coverage. Figure 7 shows such a calibration obtained using a retarding grid analyzer with 7 volts peak-to-peak modulation and ^{14}C-benzene deposited at 240-350°C. It can be seen that a C_{273}/Pt_{237} peak-to-peak height ratio (I_{273}/I_{237}) of two corresponds to approximately one carbon atom per surface platinum atom. More generally for coverages of less than one monolayer the number of carbon atoms per surface platinum atom is given empirically by C/Pt=0.62 (±15%) I_{273}/I_{237}.

Time dependent studies of adsorbate residence times, rehydrogenation kinetics, and hydrogen transfer kinetics is a unique and important application for this radiotracer technique. As an example, Figure 8 compares the rehydrogenation behavior of ^{14}C-benzene chemisorbed on Pt(111) at 60 and 300°C. In the presence of one atmosphere of flowing hydrogen, ^{14}C-benzene chemisorbed at 60°C rehydrogenates completely at 75°C in a period of about 25-30 minutes. The first order decline in the surface concentration by radioactive species corresponds to an initial rehydrogenation rate of about 2×10^{-4} molec site^{-1} sec^{-1}. On the other hand, ^{14}C-benzene chemisorbed on Pt(111) at 300°C cannot be completely removed by rehydrogenation (within 2 hours) even at temperatures as high as 400°C. Rehydrogenation of this more strongly chemisorbed carbon deposit proceeds in at least two distinct stages. The more rapid initial stage (10^{-4} - 10^{-3} molec site^{-1} sec^{-1}) displays an apparent activation energy of 12±4 kcal/mole (8). The very slow later stage(s) of rehydrogenation ($<10^{-4}$ molec site^{-1} sec^{-1} at 400°C) appear to represent the gasification of graphitic carbon as described in more detail elsewhere (8). Similar (two-stage) rehydrogenation behavior was recently reported by Krebs and Bonzel (10) for the gasification of carbon deposited on iron foils at 287°C.

General Remarks

A few additional remarks are appropriate in order to place in context the capability of the radiotracer technique described in this work. The absolute sensitivity of the technique and the uncertainty of the counting statistics are derived from the total counts for adsorbed species and background. The total counts depend on several factors including the crystal surface area, the detector efficiency, the counting time, and the specific radioactivity of the adsorbed species. While many hydrocarbons and other molecules that contain carbon-14 are commercially available with specific activities ranging up to about 64 mc mmole^{-1} (carrier free), a nominal value of 10 mc mmole^{-1} is more common. Assuming this level of radioactivity, a crystal surface area of 25 mm^2, a background of 3 cpm, and a detection efficiency of 3%, a series of simple calculations reveals that surface concentrations of 1×10^{13}, 5×10^{13}, and 1×10^{14} molec cm^{-2} can be determined in a 20 minute count with standard deviations of 23%, 10%, and 4%, respectively. Alternatively, 1×10^{14} molec cm^{-2} can be counted for only four minutes with a standard deviation of 10%. These statistics can be improved by using longer counting times, a higher specific radioactivity, or a larger area detector. It is, therefore, clear that the radiotracer technique is a very sensitive method for general surface analysis studies. Surface coverages at 1% of a monolayer can be determined non-destructively with a high level of accuracy.

In UHV applications, surface barrier detectors offer several notable advantages over thin window Geiger counters described previously (4,11). For low energy betas, surface barrier detectors are generally superior to gas counters because the window thickness is smaller, the detector is more compact, and the problems of window rupture or gas stability with time due to decomposition or diffusion through the window are absent (7). Because it is compact and rotatable, the solid state device can also be used easily in conjunction with other surface analysis methods. The primary disadvantage of the surface barrier detector is its lower efficiency (arising from the counting geometry and the need to eliminate noise pulses) which may necessitate longer counting times.

While the present discussion has been restricted to ^{14}C-radiotracers, it is important to note that many other elements possess radioisotopes that are suitable for surface studies using the same counting system. Table I lists several of these isotopes along with their half-lives and the maximum energy for their beta emission.

Conclusion

A novel counting has been developed that permits radiotracer studies to be carried out in UHV in connection with adsorption and catalysis studies on small surface area single crystal samples. The absolute sensitivity of this radiotracer technique ($\lesssim$1% of a monolayer ^{14}C) is comparable to or exceeds that of other non-destructive surface analysis methods. The technique provides valuable insights into surface reactions not obtainable by other methods.

Acknowledgement

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References

1. S.V. Norval, S.J. Thompson, and G. Webb, Appl. Surf. Sci. 4, 51 (1980).
2. B.H. Davis, J. Catal. 29, 398 (1973).
3. P. Tétényi and L. Babernics, J. Catal. 8, 215 (1967).
4. K. Klier, Rev. Sci. Instr. 40, 1525 (1969).
5. K. Klier, A.C. Zettlemoyer, and H. Leidheiser, J. Chem. Phys. 52, 589 (1970).
6. D.W. Blakely, E. Kozak, B.A. Sexton, and G.A. Somorjai, J. Vac. Sci. Technol. 13, 1091 (1976).
7. Surface Barier Detector Operating Manual and Technical Bulletin, E.G. & G. Ortec Corp., and references therein.
8. S.M. Davis, B.E. Gordon, and G.A. Somorjai, to be published.
9. P.C. Stair and G.A. Somorjai, J. Chem. Phys. 67, 4361 (1977).
10. H.J. Krebs and H.P. Bonzel, Surf. Sci. 99, 570 (1980).
11. A.D. Crowell and L.D. Matthews, Surf. Sci. 7, 79 (1967), and references therein.
12. G. Friedlander, J.W. Kennedy, and J.M. Miller, Nuclear and Radiochemistry, Wiley, New York, 1964.

Figure Captions

Figure 1. Block diagram showing the experimental arrangement and counting electronics for radiotracer studies using a surface barrier detector in an ultrahigh vacuum chamber. An expanded cross-section of the surface barrier detector is also shown (7).

Figure 2. Schematic diagram of the detector mounting assembly showing the detector offset along with the output/bias connection and provisions for cooling the detector with circulating water or nitrogen.

Figure 3. Carbon-14 beta spectra measured with a surface barrier detector at two lower discriminator energies (ca. 10 and 35 keV).

Figure 4. Plot of cpm^2/Bkg as a function of the lower discriminator energy obtained for the surface barrier detector using a ^{14}C-polymethylmethacrylate source.

Figure 5. Efficiency calibration (cpm/dpm) for the surface barrier detector obtained by depositing thin films of ^{14}C-polymethylmethacrylate onto a platinum single crystal surface. Self-adsorption by the polymer is negligible for the range of film thickness investigated.

Figure 6. Absolute surface concentrations determined as a function of the adsorption temperatures for ^{14}C-benzene chemisorbed on a (111) platinum single crystal surface (1 L=10^{-6} Torr sec uncorrected for ion gauge sensitivity).

Figure 7. Absolute Auger calibration for surface carbon coverage on platinum obtained by the radiotracer method using ^{14}C-benzene chemisorbed on Pt(111) at 240-350°C.

Figure 8. Radiotracer decay curves illustrating the rehydrogenation of ^{14}C-benzene chemisorbed on a (111) platinum single crystal surface. In the left frame, ^{14}C-benzene was chemisorbed at 60°C and rehydrogenation was carried out in 1 atm H_2 at 75°C. In the right frame, rehydrogenation was carried out at the indicated temperatures following preadsorption of ^{14}C-benzene at 300°C.

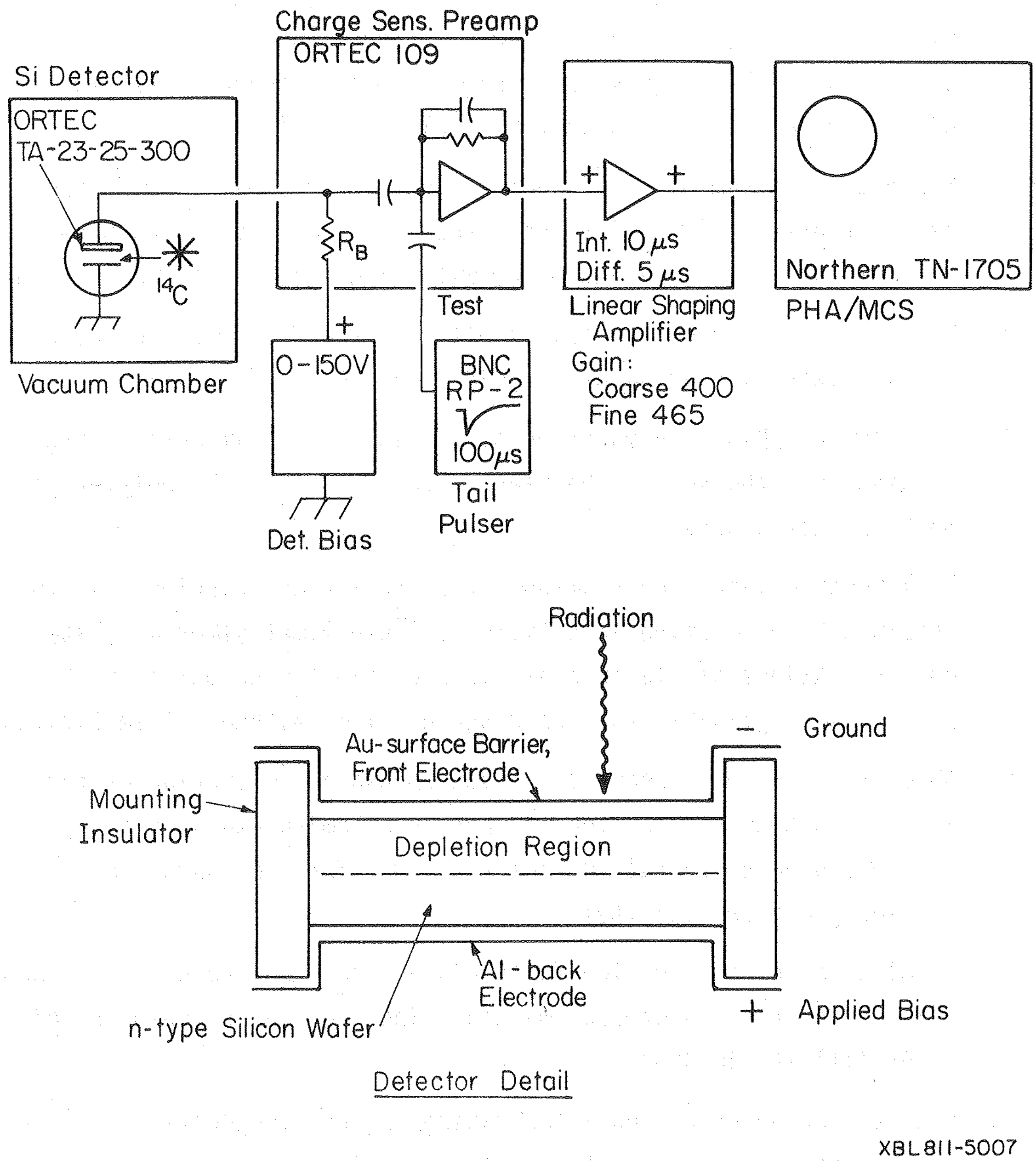
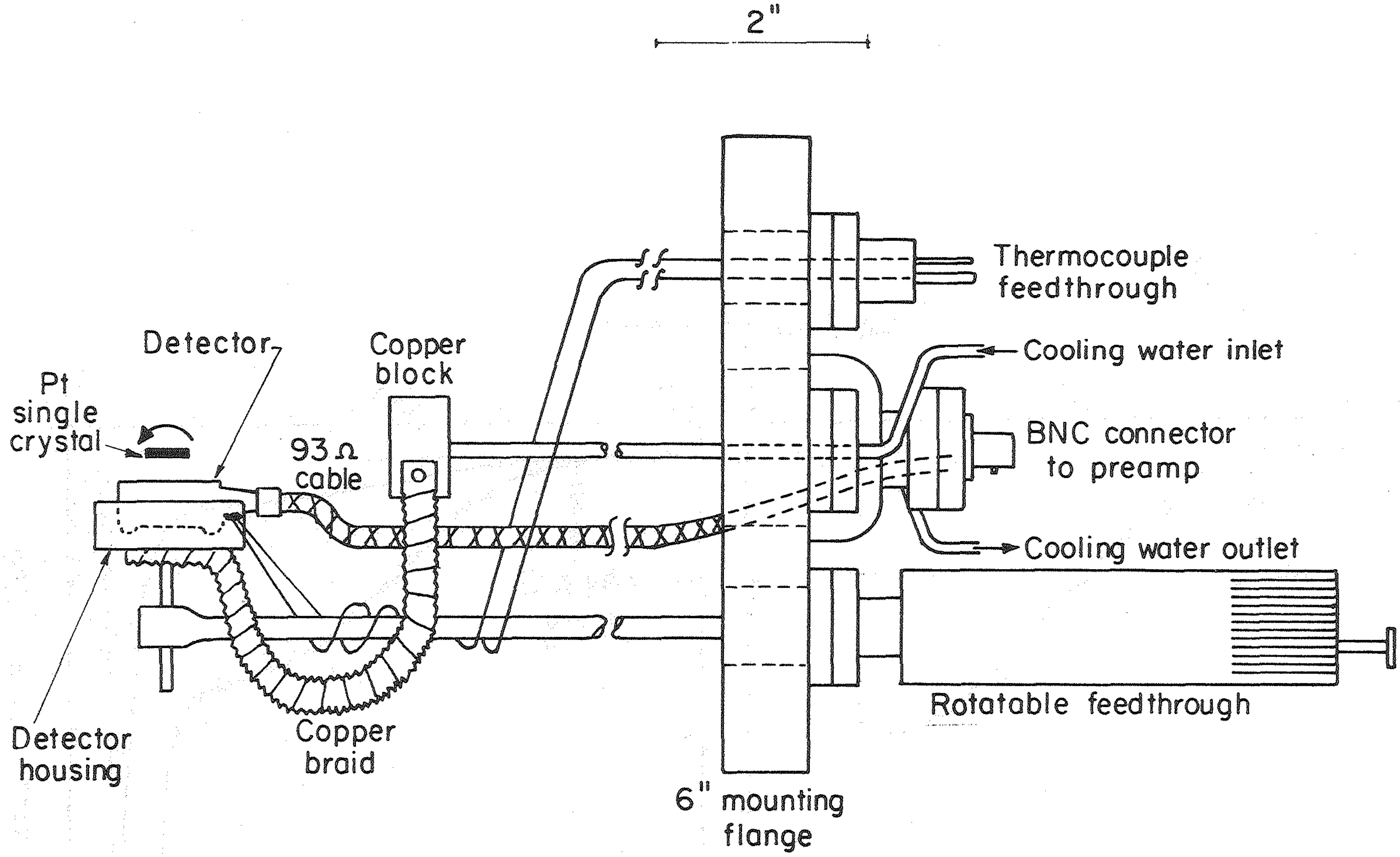
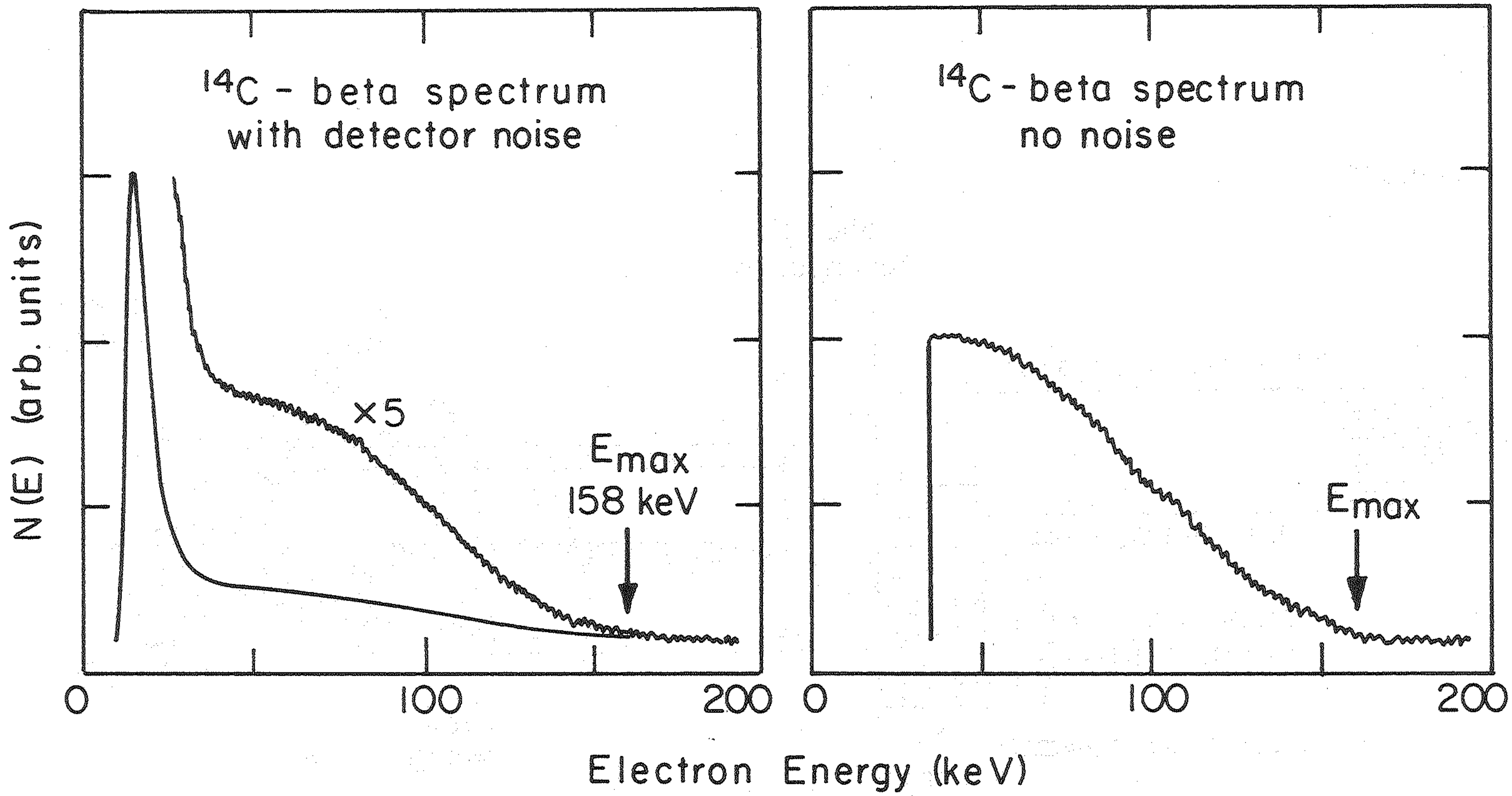

Charge Sens. Preamp
ORTEC 109
Si Detector
ORTEC
TA-23-25-300
^{14}C
R_B
Vacuum Chamber
0-150V
Det. Bias
Test
BNC
RP-2
100μs
Tail
Pulser
Int. 10 μs
Diff. 5 μs
Linear Shaping
Amplifier
Gain:
Coarse 400
Fine 465
Northern TN-1705
PHA/MCS
Radiation
Ground
Au-surface Barrier,
Front Electrode
Mounting
Insulator
Depletion Region
Al - back
Electrode
n-type Silicon Wafer
Applied Bias
Detector Detail
XBL 811-5007

Fig.1



XBL 811-5001

Fig. 2



XBL811-5002

Fig.3

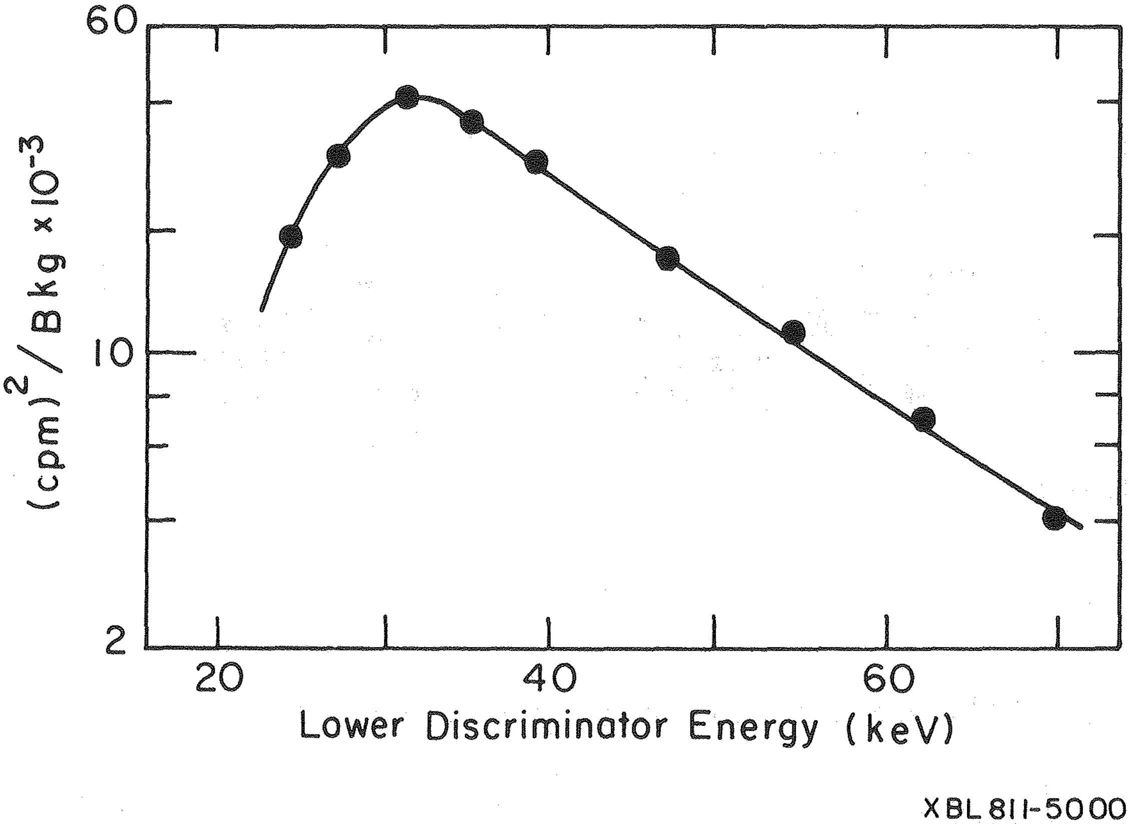

60
10
2
$(cpm)^2$/Bkg ×10^{-3}
20
40
60
Lower Discriminator Energy (keV)
XBL 811-5000

Fig.4

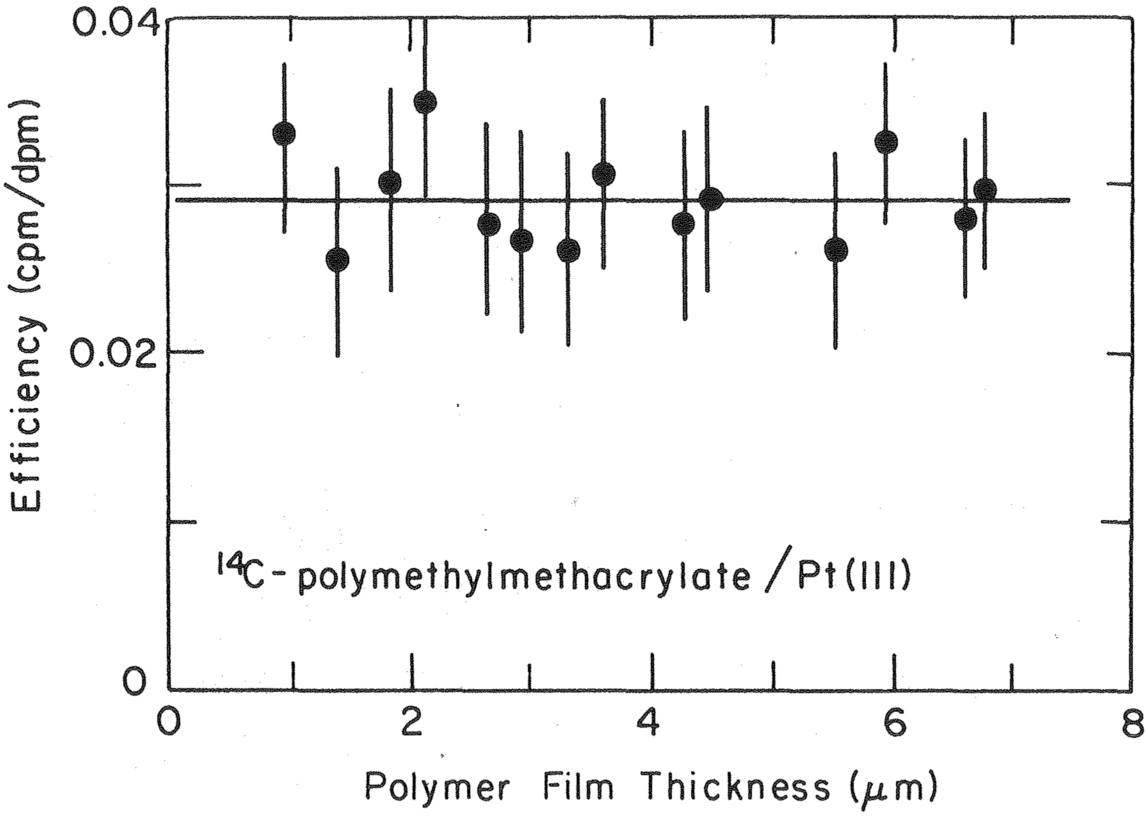


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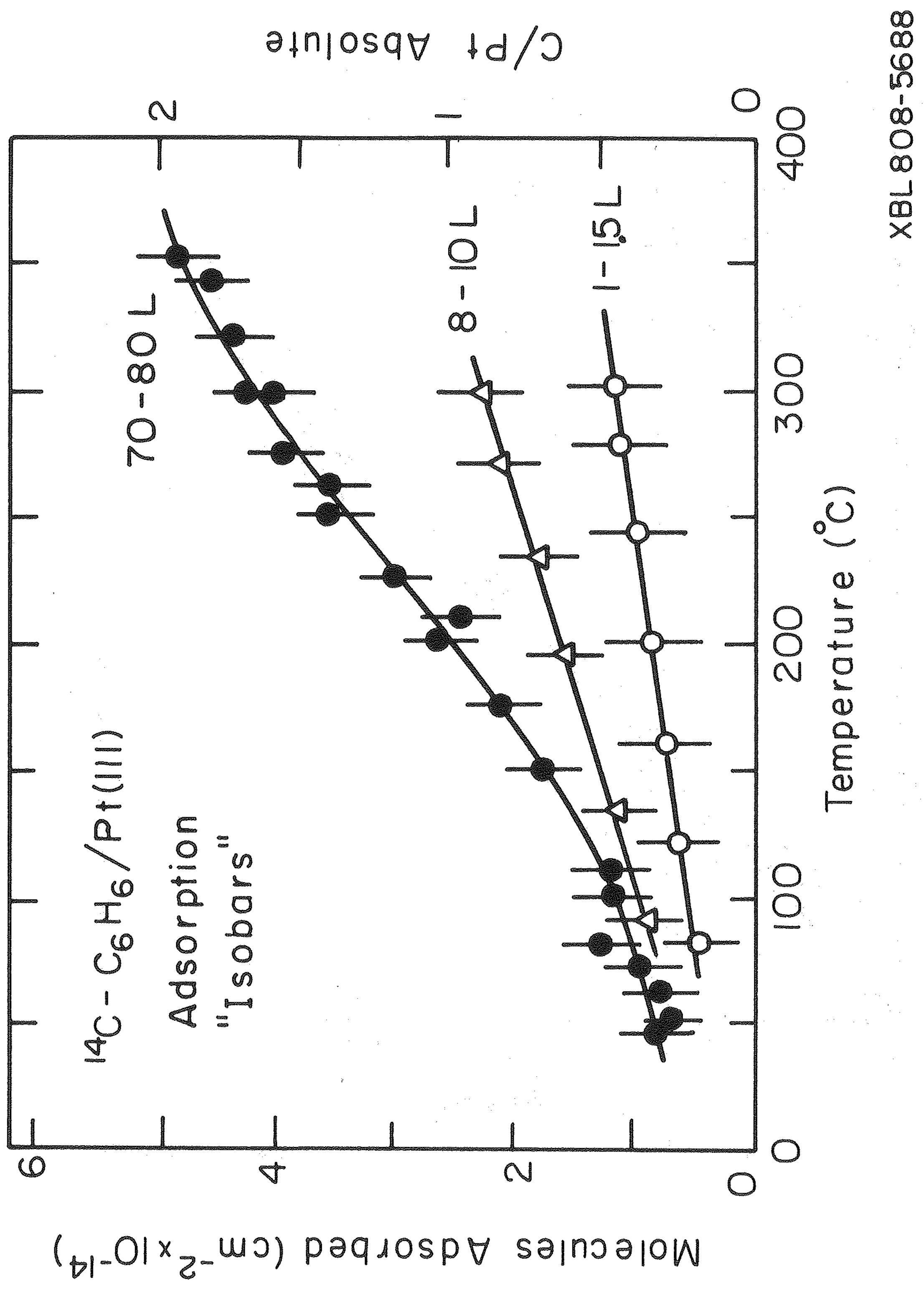
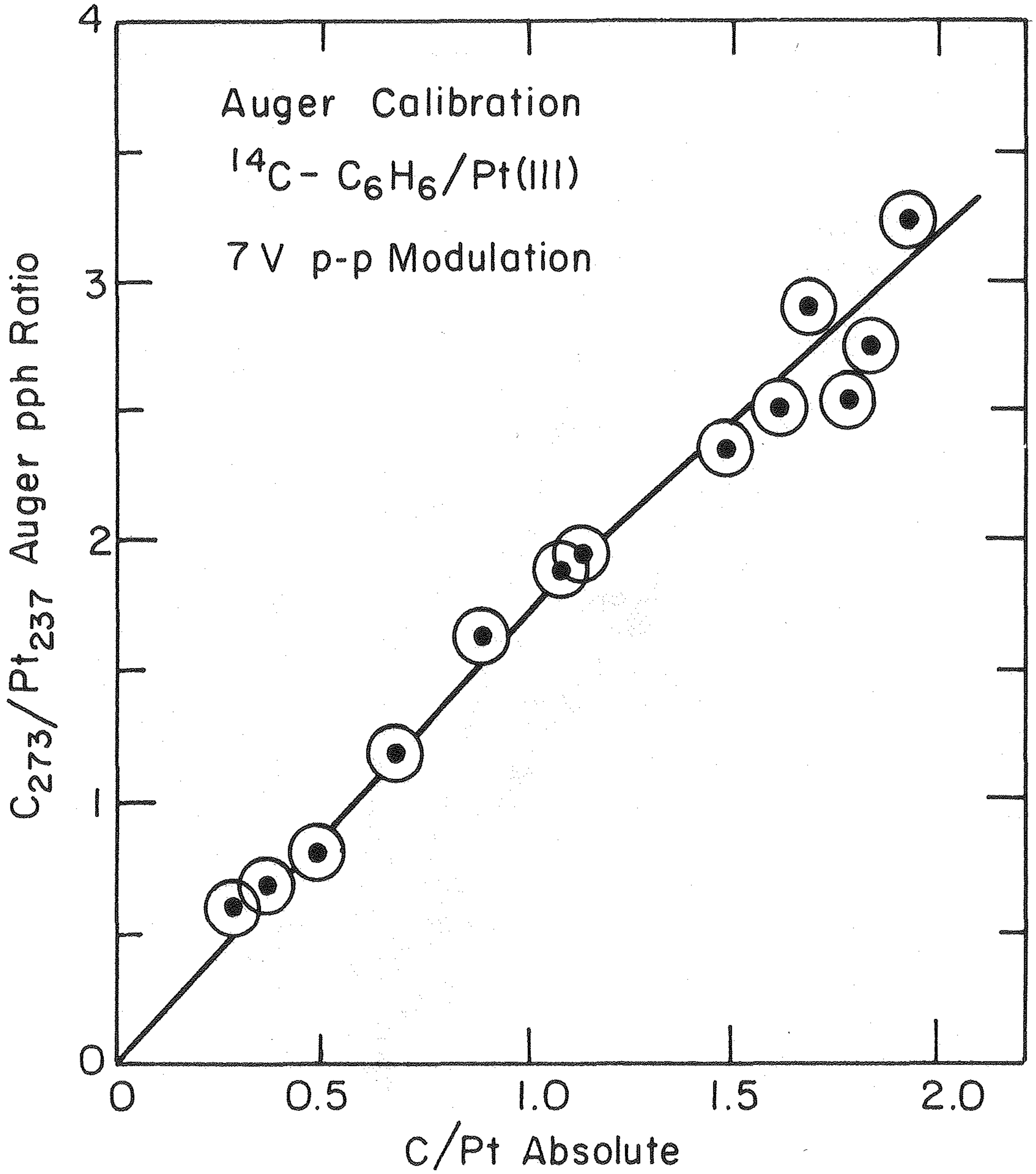
Fig.5



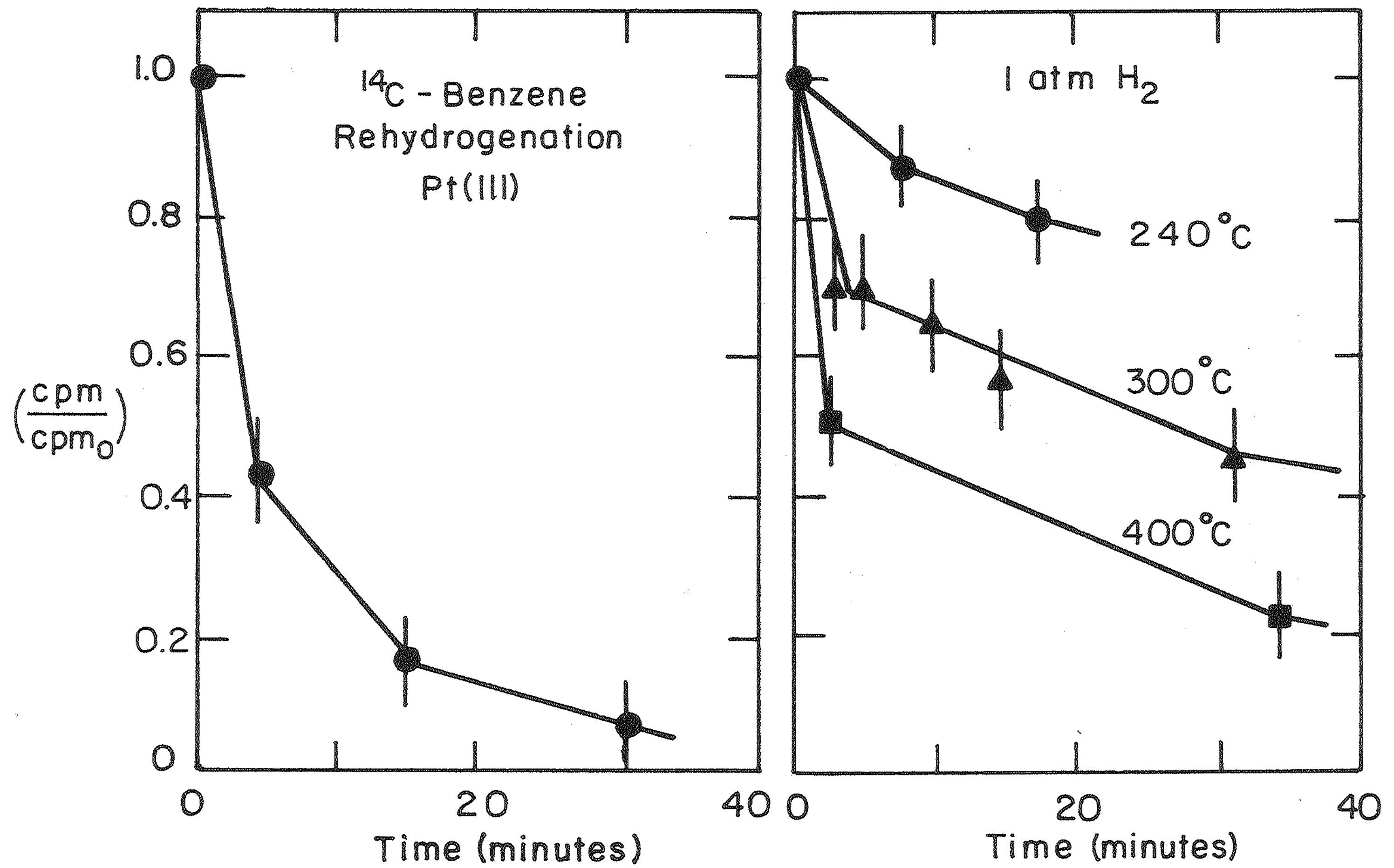
$^{14}C-C_6H_6/Pt(111)$
Adsorption
"Isobars"
70-80 L
8-10 L
1-1.5 L
Temperature (°C)
Molecules Adsorbed ($cm^{-2} \times 10^{-14}$)
C/Pt Absolute
XBL 808-5688

Fig. 6



XBL 808-5689

Fig.7



XBL 808-5691A

Fig. 8

TABLE I.

Partial Listing of Radioisotopes Suitable for Surface Studies Using a Surface Barrier Detector.[12]

Isotope	E_{max}(keV)	Half-life (yr)
^{14}C	158	5720
^{22}Na	544	2.6
^{26}Al	1160	7.4×10^5
^{32}Si	210	710
^{35}S	167	0.24
^{36}Cl	714	3.0×10^5
^{137}Cs	510	30